Nanoscale Res Lett (2008) 3:45–48
DOI 10.1007/s11671-007-9112-2

NANO PERSPECTIVES

Effect of Dopant on the Nanostructured Morphology of Poly (1-naphthylamine) Synthesized by Template Free Method

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Received: 15 September 2007 / Accepted: 30 November 2007 / Published online: 7 December 2007

Abstract The study reports some preliminary investigations on the template free synthesis of a *scantly* investigated polyaniline (PANI) derivative—poly (1-naphthylamine) (PNA) by template free method in presence as well as absence of hydrochloric acid (HCl) (dopant), using ferric chloride as oxidant. The polymerization was carried out in alcoholic medium. Polymerization of 1-naphthylamine (NPA) was confirmed by the FT-IR as well as UV–visible studies. The morphology and size of PNA particles was strongly influenced by the presence and absence of acid which was confirmed by transmission electron microscopy (TEM) studies.

Keywords Poly (1-naphthylamine) · Alcohol · Transmission electron microscopy · Morphology · Nanostructure

Introduction

Scientific and technological interest in studying nanomaterials has *spurred* to develop conducting polymeric nanostructures, using reliable and scalable synthetic methods to provide better performance of these materials in the established areas of corrosion, sensors, batteries, and EMI shielding [1–4]. Chemical oxidative polymerization of aniline is the traditional method for preparing polyaniline in bulk [5]. In the aniline polymerization reaction, an acidic solution is needed to enhance the head-to-tail coupling between aniline monomers. Typically a strong mineral acid such as hydrochloric, sulphuric, nitric, perchloric or phosphoric acid is used at a high concentration (1.0 M) for the preparation of Polyaniline (PANI) [5]. It has been reported that the diameter of the nanofibres *so formed* is strongly *influenced* by the dopant used in the polymerization [5]. Polyaniline prepared by using HCl *is* highly aggregated and contains mostly irregularly shaped agglomerates which deteriorate the desired properties of the polymer. Substituted polyanilines continues to be an emerging research area of great interest since these polymers *hold* the potential to improve upon the properties of polyaniline. Scarce literature is available on the chemical synthesis of poly (1-naphthylamine) (PNA)—a polyaniline derivative. Moon et al. [6] first reported the chemical synthesis of poly (1-aminonaphthlaene) and poly (aminoanthracene) using H_2O_2/Fe^{2+} system. Shaffie et al. [7] carried out the chemical oxidative polymerization of poly (1-naphthylamine) using potassium persulphate, and the conductivity of the polymer was reported to be in the range of ~ 0.83 Scm^{-1}. Recently, Shan et al. [8] synthesized PNA via enzymatic polymerization using horse dish peroxidase. Surprisingly, none of the studies mentioned above have reported the nanoscale synthesis of PNA.

This study reports some preliminary investigations on the template free synthesis of nanostructured PNA with a view to obtain an agglomerate free nanostructured conducting polymer. The effect of hydrochloric acid on the agglomeration of PNA is investigated by spectral as well as morphological studies.

Experimental

Chemicals: Naphthylamine (Loba Chemie, India) was purified prior to use. The monomer was sublimed at 120 °C

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and recrystallized in ethanol. Ethyl alcohol, cupric chloride, *N*-methyl pyrolidinone (NMP) (Qualigen, India) were of analytical grade and were used as such.

Synthesis of Poly (1-naphthylamine)

1-Naphthylamine (NPA) monomer (0.1 M) was dissolved in a mixture of ethyl alcohol (10 mL) and 1N HCl (10 mL) at room temperature. The solution was purged in nitrogen for 1 h. Cupric chloride (0.1 M) dissolved in ethyl alcohol (5 mL) was then added to the solution of 1-naphthylamine with slow stirring at 0 °C. A violet coloured dispersion appeared as polymerization progressed. The reactor flask was cooled to −5 °C to obtain a purple glassy phase under static conditions for 48 h between −5 and −7 °C. The purple-black-coloured glassy phase turned into suspension after holding for 30 min at room temperature. It was washed thoroughly with distilled water and methyl alcohol to remove oligomers, metal ions and other impurities. Further purification of the polymer was done through soxhlet extraction using methyl alcohol for a period of 16 h to remove oligomeric fractions and other impurities. Resulting powder was then dried under vacuum at 50 °C for 72 h. Similar procedure was adopted for the synthesis of PNA in ethanol medium without HCl.

Characterization

FT-IR spectra of the powdered polymers were taken in the form of KBr pellets on spectrometer model Perkin Elmer 1750 FT-IR spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT, USA). UV–visible spectra were taken on Perkin Elmer lambda EZ-221 of the solutions of polymers prepared in NMP. Transmission electron micrographs were taken on Morgagni 268-D TEM, FEI, USA. The samples were prepared by depositing a drop of well diluted polymer suspension onto a carbon (1 0 0)-coated copper grid and dried in an oven at 55 °C for 2 h. Conductivity measurements were performed by standard four-probe method using Keithley DMM 2001 and EG&G Princeton Applied Research potentiostat model 362 as current source. Pressed pellets of polymers were obtained by subjecting the powder to a pressure of 50 kN. The error in resistance measurements under these conditions was less than 2%.

Result and Discussion

FT-IR Spectral Analysis

The FT-IR spectra of PNA, synthesized in absence of HCl, Fig. 1a, show a broad NH-stretching vibration peak around

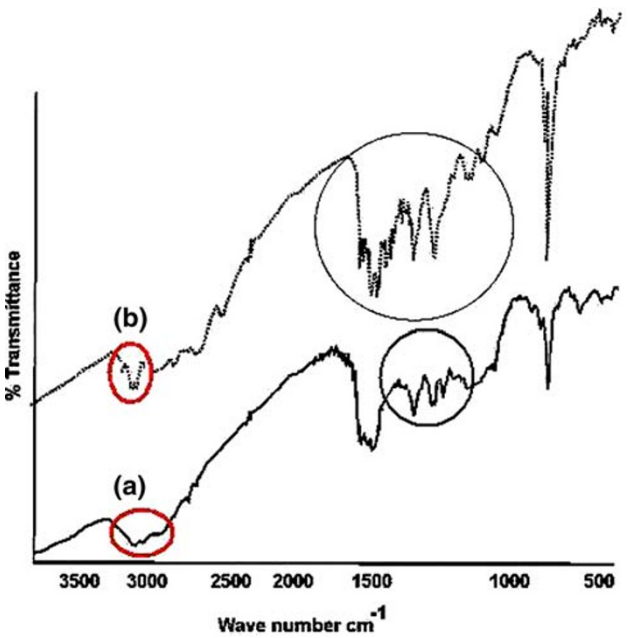

Fig. 1 FT-IR spectra of PNA synthesized (**a**) in absence of HCl (**b**) in presence of HCl

3,448 cm^{-1}, which confirms intense hydrogen bonding between PNA and ethanol. The absorption peaks corresponding to imine stretching mode appear at 1,718 and 1,654 cm^{-1}, while the peak at 1,593 cm^{-1} is assigned to the N = Q = N, quinonoid ring, skeletal vibrations. The peak at 1,512 cm^{-1} appears due to N–B–N, benzenoid ring, skeletal vibrations [9] while the CN vibration peaks are observed at 1,400, 1,314, and 1,261 cm^{-1}. The peak at 1,153 cm^{-1} is attributed to BNH^{+} = Q and B–NH–B vibrations .The presence of peaks at 764 cm^{-1} is consistent with the polymerization of NPA through N–C(4) linkages. The steepness of the base line between 2,000 and 3,000 cm^{-1} also indicates polymerization [9].

As compared to the above spectra, the FT-IR spectra of PNA synthesized in the presence of HCl, Fig. 1b, shows NH-stretching vibration peak centred at 3,370 cm^{-1} for a secondary amine. The absorption peaks of imines-stretching mode are observed at 1,654 and 1,638 cm^{-1} while the multiple peaks at 1,596 and 1,570 cm^{-1} are assigned to the N = Q = N, quinonoid ring, skeletal vibrations. The peaks at 1,508 and 1,452 cm^{-1} appear due to N–B–N, benzenoid ring, skeletal vibrations. The CN vibration shows up at 1,400 and 1,302 cm^{-1}. The $B–NH^{+}$ = Q and B–NH–B vibration peak is noticed at 1,156 cm^{-1}. The presence of strong peak at 766 cm^{-1} is consistent with the polymerization of NPA through N–C(4) linkages while the peak at 790 cm^{-1} exhibits N–C(5) coupling between neighbouring PNA rings [9].

It can be concluded that the presence of acidic conditions strongly influences the conformation of the PNA

chains. In absence of HCl, hydrogen bonding takes place between the PNA and ethanol. The PNA chains in this case, therefore, contain larger number of quinonoid units predominantly linked through N–C(4) linkages. This is evident from the spectra, Fig. 1a, which show the presence of more quinonoid vibration peaks than the benzenoid vibration peaks. However, all peaks in this case are well formed indicating a well-ordered conformation of PNA.

UV–Visible Studies

The UV–visible spectra of PNA in NMP, Fig. 2a, b, shows pronounced peaks at 350 nm in the UV range and 590 nm as well as 600 nm in the visible range. The peaks in the UV range are assigned to Π-Π* transitions in the NPA units whereas the peaks in the visible range are assigned to the polaronic transitions. Similar transitions of electrochemically synthesized PNA have been observed by Schmidt et al. [10]. The polaronic transition peak observed around 600 nm appears to be highly pronounced and broad in case of PNA synthesized in HCl, but in the absence of HCl, the peak appears to be of far lower intensity. A "compact coil" structure is observed in both cases. A small red shift is observed in case of PNA prepared in HCl, which could be attributed to the conformational changes in PNA chains upon doping with later. It appears that doping of PNA with HCl enhances the polaron formation which causes a red shift as well as enhancement in the intensity in the peak observed around 590 nm. The conductivity of PNA in presence of HCl was found to be in the conducting range, 6.1×10^{-4} Scm^{-1}, while in absence of HCl, it was found to be in the semi-conducting range, 8.7×10^{-6} Scm^{-1}.

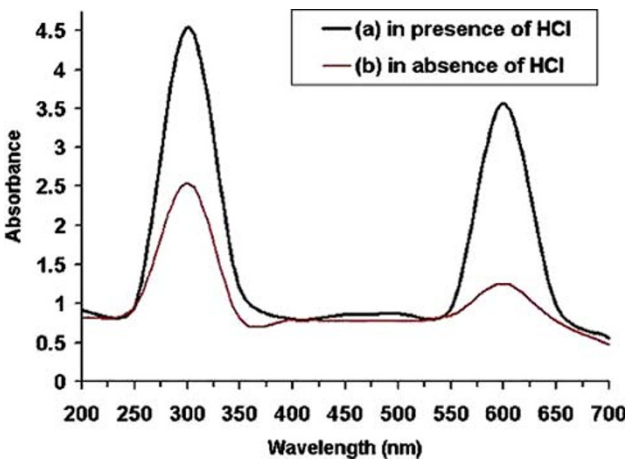

Fig. 2 UV–visible spectra of PNA

TEM Analysis

The TEM image of PNA nanostructures synthesized in absence of HCl, Fig. 3a, reveals a well-interconnected dense network structure of PNA nanoparticles with diameter in the range of 6–10 nm. The particles appear to be of uniform sizes. The micrograph also reveals a highly organized granular structure of PNA. The strong intra and intermolecular H-bonding interactions in PNA lead to extensive coiling of the polymer chains resulting in granular morphology. However, in presence of HCl, Fig. 3b, we observe that the ordering is entirely lost and a random morphology of large spherical particles of varying sizes is observed; the later being in the range of 20–30 nm. The spectral investigations also highlight the differences in the conformation, which govern the extent and nature of coiling of the PNA chains resulting in different morphologies. In the absence of HCl (undoped state), the PNA nanoparticles undergo intermolecular hydrogen bonding with ethanol that acts as a "pseudo template" and promotes the formation of

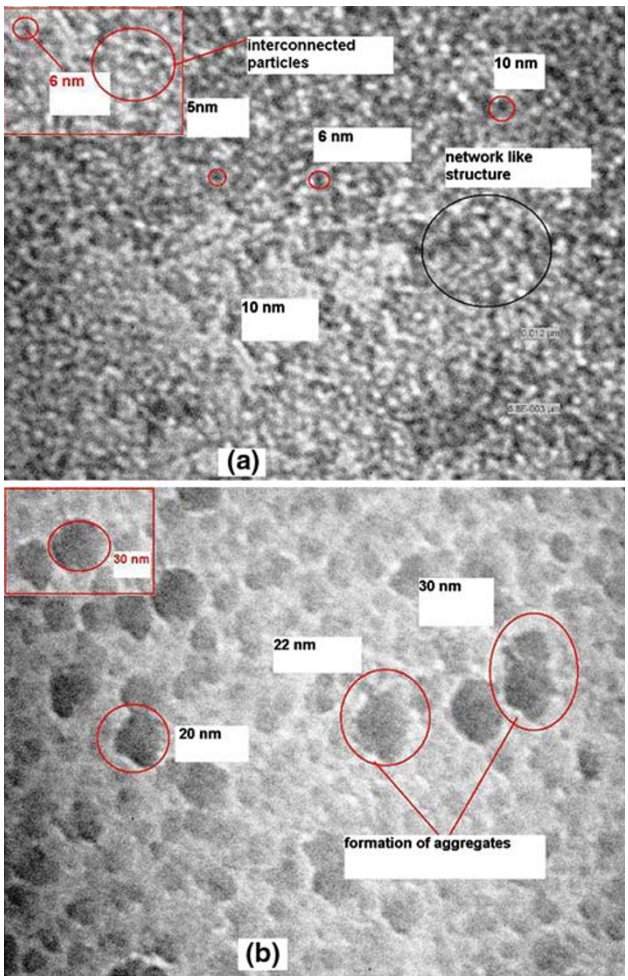

Fig. 3 TEM micrographs of PNA synthesized (**a**) in absence of HCl (**b**) in presence HCl

more compact, uniform nanostructured morphology. In presence of HCl, PNA exhibits reduced polarity and poor affinity towards ethanol [11, 12]. Furthermore, the presence of HCl as dopant increases the average diameter of the nanoparticles resulting in agglomeration which disrupts the "interconnected network" like morphology of PNA [13].

Conclusion

The synthesis of nanostructured PNA described is this article is very facile and robust which does not require any extra structural directing agents or template removing steps. Hydrochloric acid when used as a dopant plays a significant role in deciding the morphology of the nanostructure of PNA. The aggregation of nanoparticles can be prevented by avoiding the use of highly acidic dopants such as HCl as well as by using alcohol as a medium for polymerization of conducting polymers. These findings may provide valuable information in the template free synthesis of many other nanostructures. The investigations on influence of other parameters such as polymerization temperature, reaction time, mechanical agitation, and choice of oxidant, are under progress in our laboratory and will be published soon.

Acknowledgement This work was funded by CSIR through grant No. 01/(1953)/04/EMR-II. The authors wish to thank the CSIR for its financial support.

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